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MEMORANDUM

TO: John Sanders, Chief
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Department of Pesticide Regulation

FROM: Jeffrey P. Cook, Chief
Quality Management Branch
Monitoring and Laboratory Division

DATE: May 25, 2001

SUBJECT: FINAL PROTOCOL FOR THE 2001 CHLOROPICRIN APPLICATION AIR MONITORING

Attached is the final "Protocol for Air Monitoring Around a Bed Fumigation Application of Chloropicrin, June, 2001". We received and appreciate your comments (May 23, 2001, electronic mail, Segawa to Mongar) on the draft protocol and have made changes as appropriate.

If you or your staff have questions or need further information, please contact me at 322-3726 or Kevin Mongar at 322-2249.

Attachment

cc: Randy Segawa, DPR (w/Attachment)
Shifang Fan, DPR (w/Attachment)
Richard J. Sommerville, San Diego County Air Pollution Control District
Kathleen A Thunder, San Diego County Agricultural Commissioner (w/Attachment)
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State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for Air Monitoring Around a Bed Fumigation Application of Chloropicrin June 2001

Prepared by
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Quality Management Branch
Monitoring and Laboratory Division

Date: May 24, 2001

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for Air Monitoring
Around a Bed Fumigation Application
of Chloropicrin
June 2001

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (June 28, 2000 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide chloropicrin around a bed fumigation application, tentatively scheduled to be conducted in June 2001. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The DPR has requested that a chloropicrin application where methyl bromide is also being used be selected for the monitoring study. The DPR will collect samples for methyl bromide, which will be analyzed by the California Department of Food and Agriculture's pesticide laboratory. This protocol will only address the sampling for chloropicrin (i.e., will not address the DPR sampling/analysis for methyl bromide).

The sampling and analysis will follow the quality assurance guidelines described in Attachment I, "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version).

The sampling and analysis will follow the draft procedures outlined in this protocol as well as the procedures described in Attachment II, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector".

II. Sampling

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 90 standard cubic centimeters per minute (sccpm). Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are transported (driven) to the ARB laboratory in Sacramento. DPR recommends a target 24-hour estimated quantitation limit (EQL) for chloropicrin of 0.1 ug/m^3.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter, train support, and a 12 volt DC vacuum pump (see Figure 1). Each tube is prepared in the field by breaking off each sealed glass end and then immediately inserting the tube into the fitting. The tubes are oriented in the sample train with a small arrow printed on the side of each tube indicating the direction of flow. Rotameters with a range of 0-240 ccpm will be used to control the flow for sampling. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-100 sccpm. The mass flow meter has been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period with the sampling tubes installed. Any change in flow rates will be recorded in the field logbook (see Attachment IV). The pesticide sampling procedures for adsorbent tubes are included as Attachment III. The sampling schedule consists of samples collected during daylight and overnight periods as shown below in Table 1.

Table 1
Application Sampling Schedule

Sample period begins	**Sample duration time**
Background (pre-application)	24 hours if possible; minimum 12 hours (if <24 hours must meet 24-hour EQL)
During application and post –application	Start of application until 1 hour before sunset
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour before sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour before sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

In the event that application occurs at night, the alternate day-night schedule will be followed. If the fumigation takes two or more days, samples will be collected during the overnight period separating the applications and the above overnight/daytime schedule will then be followed from the last day of application.

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

Table 2
Application Information

Location:	South side of Via de la Valle Road, Del Mar
Field Size:	21 Acres
Product Applied:	50% methyl bromide, 50% chloropicrin (by weight)
Type of Application:	Bed tarpaulin fumigation
Commodity:	Soil, tomato pre-plant
Application Rate:	175 lbs. each Mebr and chloropicrin per acre
Grower/Applicator:	Leslie Farms/TriCal

DPR staff, along with the San Diego County Agricultural Commissioner's office staff, have coordinated the selection of the study site and the test dates and have obtained permission from the grower (and any other land owners where samplers may be located). Chloropicrin/methyl bromide bed-tarpaulin applications typically proceed at a pace of about one acre per hour or about 10 acres per day per application rig.

A minimum of 8 samplers will be positioned, one on each side of the field and one at each corner. A 9th replicate sampler will be collocated at one position (downwind site). Ideally, samplers should be positioned 200 feet from the field; however, site conditions will dictate the exact placement of samplers.

In regard to field data, the monitoring report will include: 1) a record of the positions of the monitoring equipment with respect to the field, 2) the application start location, 3) the direction of crop rows 4) how the field was divided to treat if over several days, 4) a drawing of the monitoring sites showing the precise location of the meteorological equipment, trees, buildings and other obstacles, 5) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, and air temperature and comments regarding degree of cloud cover, 6) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North), and 7) the start and end time of the application.

III. Analysis

The draft sampling and analysis method and validation results for the sampling and analysis of chloropicrin are included as Attachment II. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour sample at 90 sccpm, the MDL and EQL would be 30.5 ng/m^3 and 152 ng/m^3, respectively. The DPR target EQL was 100 ng/m^3. The analyses will be performed by the ARB laboratory in Sacramento.

IV. Field Quality Assurance

Field Quality Control for the application monitoring will include the following:

1) Four field spikes will be obtained by sampling ambient air at the application monitoring site for between 12 and 24 hours. The field spikes will be obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for chloropicrin in the adsorbent tube samples have not yet been determined.

2) Four trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

3) Four lab spikes will be prepared at the same level as the field and trip spikes. The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.

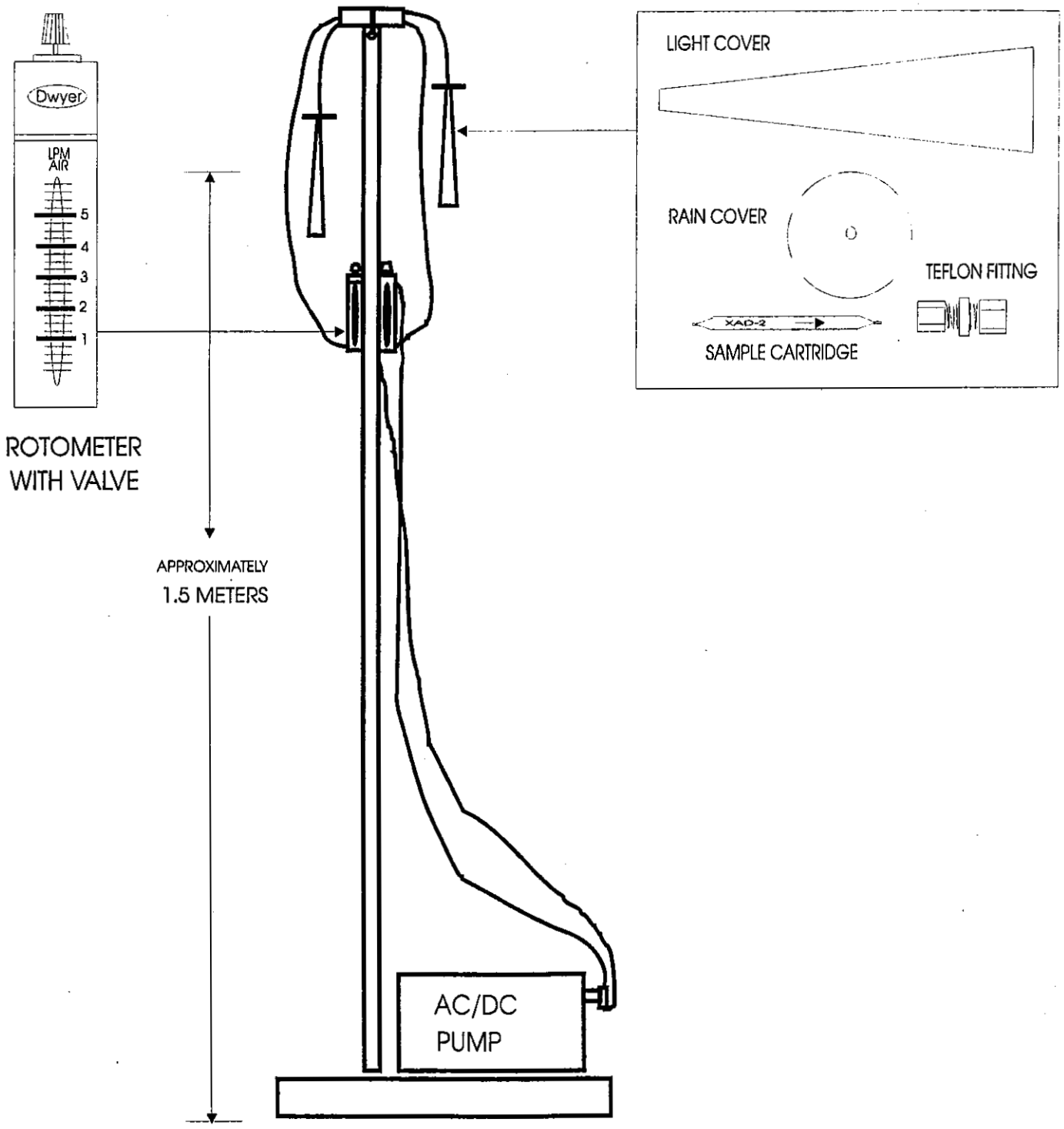
4) Collocated (replicate) samples will be taken for all sampling periods (except the background period) at one sampling location (downwind).

5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

VII. Personnel

ARB sampling personnel will consist of staff from the Air Quality Surveillance Branch of ARB. DPR staff will collect samples for the first two application sampling periods.

FIGURE 1. SAMPLE TREE



Attachment I

Quality Assurance Plan for Pesticide Air Monitoring

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN FOR PESTICIDE AIR MONITORING

Prepared by the

Monitoring and Laboratory Division
Engineering and Laboratory Branch

Revised: May 11, 1999

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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff determines the airborne concentrations of specified pesticides following monitoring recommendations established by the DPR. This air monitoring is conducted to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The documentation of airborne concentrations is usually accomplished through two types of monitoring. The first consists of five to eight weeks of **ambient** monitoring in the general area of, and during the season of, peak use of the specified pesticide. The second is monitoring around the perimeter of a field during and for 72 hours after an **application** has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with accurate, relevant and timely air monitoring measurements of airborne pesticide concentrations. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are as follows.

(1) to establish the necessary quality control activities relating to site selection, method validation, analytical standard operating procedures (SOP), sample collection, sampling and analysis protocol, data reduction and final reports, and;
(2) to assess data quality in terms of precision, accuracy and completeness, and;
(3) to design air monitoring strategies to meet the pesticide target (estimated) quantitation levels as provided by the DPR.

II. Air Monitoring

All sampling will be coordinated through communication with the County Agricultural Commissioner's Office. The local Air Quality Management District (AQMD) or Air Pollution Control District (APCD) will be notified prior to any monitoring. Sample collection will be conducted by staff of the Testing Section or staff of the Air Quality Surveillance Branch of the ARB, or an approved ARB contractor.

A. Siting

The location and time-frame for **ambient** and **application** monitoring are based on direction provided by the DPR in their "Use Information and Air Monitoring Recommendation for Pesticide Active Ingredient" documents. These recommendations are based on historical trends (normally 2 to 3 years prior) and are submitted to the ARB by the DPR approximately 1 year in advance of intended monitoring. The recommendations direct ARB to monitor for a pesticide in specific counties during specific use periods. Pesticide use maps (historical) and histograms are used along with close coordination with staff of the County Agricultural Commissioner's Office to predict areas (and times) of use for the pesticide for the upcoming use year. Approximately one month prior to the scheduled monitoring DPR will reevaluate the historical use trends using the most recent pesticide use data available.

For selection of **ambient** monitoring sites, ARB staff work through authorized representatives of school districts, private companies or city, county or state government agencies. The probe (sampler) siting criteria for **ambient** pesticide monitoring were obtained from the U.S. EPA "Ambient Air Quality Surveillance" criteria (40 CFR, Part 58) and are listed in TABLE 1. As per the DPR monitoring recommendations, three to five sites are chosen. The monitoring objective in choosing these sites is to estimate population exposure in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). Sampling sites should be located near (in regions of) specific agricultural crops as recommended by the DPR. One additional site is chosen and designated to be an urban area "background" site which is located away from any expected applications. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground. Normally the **ambient** samplers will be located on the roof of a one-story building (e.g., at schools) with the sample cartridge located about 1.5 meters above the roof.

Probe siting criteria for placement of samplers around a pesticide **application** are the same as for **ambient** monitoring tests (TABLE I). A minimum of four samplers are positioned, one on each side of the field. A fifth sampler is collocated at one position, normally the downwind side (based on prevailing breezes). Once monitoring has begun, the sampling stations are not moved, even if the wind direction has changed. Ideally, samplers should be placed at a minimum distance of 20 meters from the perimeter of the field and should be equidistant from the field. *These requirements are nearly impossible to meet because of the physical limitations of most application sites. Twenty meters from a potential application field invariably places the sampler on another landowner's property, in another field where tractors and other equipment must operate, or into another orchard where the siting criteria cannot be met. Fences, canals, roads, ditches, railroad tracks, brush, trees, houses, barns, livestock, parked equipment, uncooperative neighbors, etc. are common obstacles. Monitors are placed as far as possible, up to 20 meters, from the field. Attempts are always made to center the samplers on the face of a side of the field. The sampler is placed to maximize the distance from the field and to avoid obstructions bordering the field. Conditions at the site will dictate the actual placement of monitoring stations.* Information is collected and reported to DPR regarding; 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that

the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees buildings and other obstacles; 3) the elevation of each sampling station with respect to the field and the orientation of the field with respect to North (identified as true or magnetic North). Determination of an appropriate site for an **application** test is based on the "recommendations" provided by the DPR. Parameters used to choose the site are:

1. crop type,
2. minimum field area of 10 acres,
3. minimum application rate (as directed by the DPR),
4. type of application (normally no preference by the DPR),
5. availability of sites on all four sides of the field which meet the criteria in Table 1 and can be sited 20 meters from the perimeter of the field (quite often this is not possible, i.e., normally 4 sites are chosen but they may not all meet the criteria), and
6. accessibility and security of the sampling sites/equipment.

Monitoring sites (fields) are arranged through communication with, and the voluntary cooperation of, applicators, growers or owners for **application** monitoring. Normally, representatives of the County Agricultural Commissioner's Office will make initial contact with the applicators/growers or will at least provide a list of possible candidates.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

Height Above Ground (Meters)		2-15
Minimum Distance from Supporting Structure (Meters)	Vertical	1
	Horizontal	1
Other Spacing Criteria		1. Should be 20 meters from trees.
		2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler.
		3. Must have unrestricted air flow 270° around sampler.
		4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

B. Schedule

Samples for **ambient** pesticide monitoring will generally be collected over 24-hour periods on a schedule of 4 samples per week (Monday through Friday) for 5 to 7 weeks. Occasionally the normal schedule will be interrupted due to holidays and make-up samples may be collected over weekends.

Individual **application** monitoring schedules will vary based on the type and length of application but will follow the schedule guidelines outlined below in TABLE 2. Ideally, the

monitoring study will include samples taken before, during and for approximately 72 hours following application.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	**Sample duration time**
Background (pre-application)	Minimum of 12 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) [1]
1 hour post-application	2 hours (or up to 1 hour before sunset) [1]
3 hour post-application	3 hours (or up to 1 hour before sunset) [1]
6 hour post-application	6 hours (or up to 1 hour before sunset) [1]
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

1 These sample duration times will be adjusted depending on length of application and time of sunset.

2 All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur all day long and over the course of two or more days. In these instances samples are collected during the first daily application, followed by a sample from end of application to 1 hour before sunset, followed by an overnight sample ending at either the start of application or 1 hour after sunrise the next morning (same for second or more application days). Following the end of the application, samples are collected according to the above schedule, starting with the 1-hour sample.

C. Meteorological Monitoring

Data on wind speed and direction, barometric pressure, relative humidity and air temperature will be collected during **application** monitoring by use of an on-site meteorological station. The meteorological data will be acquired using a data logger at a minimum of 15 minute intervals (averages). Meteorological systems will be calibrated as specified in the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring." Meteorological data are not collected for the **ambient** monitoring programs.

III. Method Validation

A. Method Detection Limit

The method detection limit (MDL) is defined as the lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and matrix.

MDL is defined as 3.14 x s; where s is equal to the standard deviation of seven replicate spiked samples (e.g., XAD sample cartridges). The spiked samples are prepared and analyzed in the same way as actual samples. The spikes should be prepared at a concentration that is between one to five times the estimated MDL.

B. Estimated Quantitation Limit

The estimated quantitation limit (EQL) is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. This EQL is defined as 5 x MDL.

C. Reproducibility

The reproducibility of the method should be determined by performing five replicates at three different concentrations. The lowest level should be at or near the EQL. The average and standard deviation of each set of replicates should be determined and reported.

D. Extraction Efficiency

Extraction efficiency is defined as the amount of pesticide recovered from a spiked sample. Three replicates at two levels and blank should be extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 will give the percent recovery. Recommended recoveries should be between 70-130%.

E. Sampling Efficiency

Sampling efficiency is determined by spiking a sample with a known amount of pesticide. The spiked sample is placed in a sampler and set to the same flow rate and time that samples are collected. At a minimum three replicate spiked samples at a concentration two times the EQL of the method and a collocated background are collected. The samples are extracted and average recovery and standard deviation of the spike samples are determined.

F. Breakthrough

Breakthrough is determined by using a two stage sampling media (usually a filter or resin). The front stage is spiked with a known quantity of the pesticide. The breakthrough study samples are normally spiked at a relatively high level, e.g., at a level that might be observed

during an application study. If time and resources permit, both low and high level spike studies are run. The backup will be the same filter or resin type and placed in series with the front filter or resin. Air is passed through the sampler at the same flow rate and sample time as a real sample (minimum sample time of 24 hours). The front and backstage are recovered and extracted separately. If breakthrough is observed then the sampling strategy must be reviewed, modified and retested before the start of a sampling project.

G. Freezer Storage Stability

Spiked samples should be stored under the same conditions as the samples and for the anticipated time that the samples are stored. Recoveries are determined. A high (either at a level expected during the application study or at the high end of the calibration curve) and a low (1 to 2 times the EQL) concentration set should be studied. A set consists of three replicate spikes each for 3 time intervals.

IV. Field Sampling Quality Control Procedures

Monitoring programs will include the following quality control procedures:

A. Sample Labels

Sample labels will be affixed either directly to the sampling cartridge or will be placed in the individual sample container (e.g., culture tube or zip-lock bag). The sample labels will include at least the following information.

1. Pesticide name and the ARB project number.
2. Log number
3. Sample I.D.
4. Monitoring Location
5. Sampling end date
6. General comments

B. Log Sheets

Field data log sheets will be used to record the sampling log number, sample I.D., start and stop dates, start and stop times, start and end flow rate, initials of individuals conducting sampling, malfunctions, leak checks (at the beginning and end of each sampling period, see Appendix I), weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Refer to Appendix I for a recommended log sheet format.

C. Chain of Custody Forms

Attached as Appendix II is a recommended format for chain of custody (COC) sheets. A COC sheet must accompany any/all samples during transport, transfer or storage. All exchanges of sample possession must be recorded. The laboratory will keep copies of the COCs and

forward the originals to the project engineer. The original COC sheets must be retained in the pesticide project file.

D. Flow Controller Calibration and Audit

Field flow controllers (rotameter, electronic flow controller or critical orifice) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard (e.g., digital bubble flowmeter or electronic digital mass flowmeter) must be verified, certified or calibrated with respect to a primary standard at least once per year by the Quality Management and Operations Support Branch (QMOSB) of ARB. Appendix V shows an example of a form to document the flow controller calibration results.

A flow audit of the field air samplers will be conducted by the QMOSB before each pesticide monitoring project. If results of this audit indicate a difference from the calibrated values of more than 10%, then the field flow controllers should be rechecked until they meet this objective. A written report of the QMOSB audit results will be included as an appendix in the final monitoring report.

Sampling flow rates should be checked in the field and noted before and after each sampling period. A separate, certified flow meter (i.e., not the one used in the sample train to control flow) will be used to check the flow. The flow rates should be checked after the initial sampling system leak check and before the "end" sampling system leak check.

E. Background Sampling

A background sample will be taken at all sites (4 sides) prior to an **application** test. The duration of the background sample should be sufficient to achieve the pesticide target 24-hour EQL, as directed by the DPR prior to the test, and must be a minimum of twelve hours and up to 24 hours if scheduling permits. This sample will establish if any of the pesticide being monitored is present in the air prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for **ambient** monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site. Detectable levels of some pesticides may be found at an urban area background site if they are marketed for residential as well as commercial/agricultural use. An example of an urban area background site is the ARB air monitoring station in downtown Fresno.

F. Collocated Samples

For both ambient and application monitoring, the method precision will be demonstrated in part by collecting samples from collocated samplers (replicate analysis of samples also relates to method precision). An additional **ambient** sampler will be collocated at each of the sampling

sites. Normally, collocated samples will be collected at each **ambient** site every Wednesday for each week of sampling. The samplers should be located at least two meters apart if they are high volume samplers (>20 Lpm) in order to preclude airflow interference. This consideration is not necessary for low flow samplers. The collocated sampler for **application** monitoring should be positioned at the downwind sampling site where the highest concentrations are expected. The collocated site is not changed after the study starts.

G. Trip Blanks

A trip blank should be included with each batch of samples submitted for analysis. This will usually require one trip blank for an **application** monitoring study and one trip blank per week for an **ambient** monitoring program. Trip blanks are prepared by opening a sampling cartridge (e.g., breaking the ends of an XAD glass tube) in the field followed by normal labeling and sample transport (i.e., along with the samples).

H. Laboratory, Trip and Field Spikes

The *laboratory, trip and field* spikes are prepared, extracted and analyzed at the same time and they are generally all spiked at the same level. The *laboratory* spikes are immediately placed in the laboratory refrigerator (or freezer) and kept there until extraction and analysis. The *trip* spikes are kept in the freezer until transported to the field. The trip spike samples are kept on dry ice in an ice chest (the same one used for the samples) during transport to and from the field and at all times while in the field except for trip spike sample log-in and labeling. The *field* spikes are stored and transported in the same way as the trip spikes. However, field spikes are obtained by sampling ambient air through the spiked cartridge at the same environmental and experimental conditions as those occurring at the time of the study.

Ambient field spikes are collocated (same location, flow rate and sampling period) with a sample collected at the urban background sampling site (to minimize background concentrations). **Ambient** field spikes are normally prepared at a level of approximately 2 times the EQL, or at a level representative of ambient concentrations.

Application study field spikes are collocated with the background samples collected at the four sides of the application site (i.e., one background and one field spike per side). **Application** field spikes are normally prepared at a level close to expected air concentrations. Field spike results are corrected by subtracting the amount of pesticide residue found in the collocated, unspiked sample before calculation of residue recoveries.

I. Transportation of Samples

All samples will be capped, placed in a sample container (e.g., culture tube or zip-lock bag) and placed in an ice chest on dry ice immediately following sample collection and labeling. The samples will remain on dry ice until transferred to the laboratory and will then be stored in the lab refrigerator or freezer. Any special handling procedures will be identified during the method validation and will be outlined in the SOP.

J. Meteorological Station Calibration

Meteorological station calibration procedures will be performed as specified by the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring."

K. Preventive Measures

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

V. Analysis

Method development and analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, a systems audit may be performed, upon request, by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis per a pesticide project. After a history of competence is demonstrated, an audit prior to each pesticide project is not necessary. However, during each pesticide project, the spiked samples discussed above should be provided to the laboratory to demonstrate accuracy and precision. These spiked samples will be prepared by qualified ARB laboratory staff.

If using GC/MS, isotope dilution is the recommended method for quantitation. Isotope dilution is where the isotope analog of the target compound is spiked to the sample prior to sample preparation. The internal standard goes through the same sample and analytical steps that the target analyte does thus compensating for losses during sample preparation and instrument variability during analysis. When no isotope is available an internal standard is recommended. An internal standard is spiked to the sample just prior to analysis. The internal standard compensates for instrument variability. If no suitable internal standard is found then an external standard method may be used.

VI. Analytical Quality Control Procedures

A. Mass Spectrometer Tuning (if MS is used)

A daily tune shall be performed using perfluorotributyl amine (PFTBA). The MS should be calibrated to optimize the MS for the mode of operation and type of pesticide analyzed. Documentation and performance criteria shall be specified in the standard operating procedure. A record of the tune for each batch should kept on file. A daily tune must be performed prior to the analysis of an analysis sequence and every 24 hours during an analysis sequence. If longer intervals between tunes are used, then the stability of the MS must be demonstrated during the method development phase and approved prior to the sample analysis.

B. Calibration

Initial Calibration

At the beginning of method development an initial multi-point calibration curve is performed to demonstrate the calibration range of the pesticide analyzed. A typical multi-point calibration consists of 5 different concentrations with a single replicate at each concentration. The calibration range usually should not exceed 40:1 with the lowest level standard at the EQL unless there is no need to measure values as low as the EQL. Depending on the linear range of the analyte, multi-points with other than 5 levels may be used although a multi-point with less than 3 levels is not permitted. Typically a linear calibration is preferred although a dynamic range using a quadratic is acceptable. For quadratic calibration curves quantitation can only be performed within the calibration range. Sample above the calibration curve must be diluted into the calibration range and reanalyzed.

Daily Calibration

Prior to the analysis of a set of samples a calibration must be performed. This calibration is called the daily calibration. The daily calibration is either a multi-point calibration or a mid-point calibration. The mid-point calibration consists of a single calibration at the mid-point of the initial multi-point calibration curve. If the mid-point is within a prescribed range (i.e., within +/- 20% of the original calibration) as determined from the initial calibration then the original initial calibration is still considered valid and the response is replaced. If the mid-point calibration is outside that range then another multi-point calibration must be performed. A calibration check at the same level is also run. If the mid-point calibration and the midpoint calibration check are within a prescribed range (i.e., +/-20%) of each other then analysis can begin. If the calibration check is outside the specified range then the problem must be rectified before analysis can begin.

C. Reagent Blanks.

A reagent (solvent) blank is performed at least for every batch of reagent used. The reagent blank uses the same solvent that was used for the sample preparation. The blank should be free of interferences. If low level contamination of the pesticide residue is found in the reagent blank (as may happen when using isotope dilution), then a reagent blank will be performed before analysis of each batch of samples. A reagent blank must be analyzed after any sample which results in possible carry-over contamination.

D. Laboratory Control Blank.

A laboratory blank is run with each batch of samples. A laboratory control blank (blank sampling media, e.g., resin cartridge or filter) is prepared and analyzed by the same procedures as used for field samples. Laboratory blank results must be no higher than 20% of the lowest value reported.

E. Laboratory Control Spike.

A laboratory control spike (LCS) is a resin cartridge spiked (at the level of the midpoint of the daily calibration runs) with a known amount of standard. The LCS is prepared and analyzed the same way as the samples. Two LCS are performed for each batch of samples. Laboratory control spikes need to be within 40% (100*difference/average) of each other and have recoveries that are +/-30% of the theoretical spiked value. If in the method development stage it is found that the differences or recoveries are larger, then they must be approved by ARB before the analysis can begin.

F. Calibration Check Samples.

A calibration check sample (CCS) is a mid-point standard run after every tenth sample in an analysis set. The purpose of the CCS is to ensure sample drift is within specified values. The CCS sample must be within +/- 25% of its theoretical value. If the standard is outside this range, then the samples associated with that calibration check sample must be reanalyzed. If in the method development stage it is found that the CCS variation is greater than 25%, then the percent variation limit used for the method must be approved by the ELB Branch Chief before the analysis can begin.

G. Duplicate Analysis.

A duplicate analysis is a sample analyzed in duplicate as a measure of analytical precision. Every tenth sample of an analysis set must be run in duplicate.

H. Standard Operating Procedures

Analytical methods must be documented in a Standard Operating Procedure (SOP) before monitoring begins. The recommended format for the SOP is provided in Appendix III. The SOP will include a discussion of all of the procedures outlined above in this section. The SOP will also include a summary of method development results as outlined in Section III above.

VII. Sampling and Analysis Protocol

Prior to conducting any pesticide monitoring, a sampling and analysis protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method (SOP included if possible).

5. Tentative test schedule and expected test personnel.

6. Safety information specific to the pesticide monitored.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Procedures which apply to all sampling projects include: (1) sample log sheets (APPENDIX I), (2) chain of custody forms (APPENDIX II), (3) sunlight and rain shields for sample protection during monitoring, (4) sample storage in an ice chest on dry ice until delivery to the laboratory, (5) trip blanks and, (6) laboratory, trip and field spikes. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

VIII. Final Reports and Data Reduction

The mass of pesticide found in each sample should be reported along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter) or ng/m^3 (nanogram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units at conditions of 1 atmosphere and 25 °C. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume.

The final report should indicate the dates of sampling as well as the dates of laboratory receipt, extraction and analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring studies are sent to the Department of Pesticide Regulation, the Office of Environmental Health Hazard Assessment, the Department of Health Services, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering and Laboratory Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building)

including the locations Range/Township/ Section. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average ("detected" results are factored in as (MDL+EQL)/2, <MDL results are factored in as MDL/2), total number of samples, number of samples above the estimated quantitation limit (EQL), number of samples "detected" and the number of samples below the MDL. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX IV). Meteorological data will be reported in 15 minute averages for the application site during the monitoring period. Meteorological and pesticide air concentration data will also be summarized as wind roses for each application sampling period. The raw meteorological data file will also be transferred to DPR on 1.44 mb floppy disk.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, collocated etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

APPENDIX I

SAMPLE FIELD LOG BOOK

SAMPLE FIELD LOG BOOK
Project: Pesticide Air Monitoring
Project #:

Log #	Sample ID	Date On/Off	Time On/Off	Start Flow	End Flow	Start Leak Check	End Leak Check	Comments	Weather o=overcast pc=partly c=cloudy k=clear	Techn. Initial

APPENDIX II

CHAIN OF CUSTODY FORM

CHAIN OF CUSTODY FORM
CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812
PESTICIDE
CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: _____
Sample/Run #: _____ Time: _____
Job Name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	

RETURN THIS FORM TO: _____

APPENDIX III

ANALYTICAL STANDARD OPERATING PROCEDURE FORMAT

ELEMENTS TO BE INCLUDED IN LABORATORY STANDARD OPERATING PROCEDURES FOR PESTICIDE AIR ANALYSIS

Engineering and Laboratory Branch
Air Resources Board
April 1999

I. SCOPE

A. Description of scope and detection limits of pesticide(s) to be analyzed.
B. Documents and references upon which method is based.
C. Definitions of any special terms must be given.

II. SUMMARY OF METHOD

A. General description of sampling and analytical procedure. Enough information should be included for an experienced analyst to readily recognize the principles of operation.

III. INTERFERENCES AND LIMITATIONS

A. Comments made here should cover both analytical and sampling problems, known and potential.

IV. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION: As specific a description as possible. Any modifications or improvements of the basic system must have an accompanying schematic. For chromatographic analysis list columns, flow rates, temperatures, detectors, amplifier ranges and attenuations, sample volumes, etc.
B. AUXILIARY APPARATUS: Provide a description of the function and operating conditions. Include a description of the sampling equipment if the equipment is specific to this method. For example, "Vacuum pump, ACME Model 62, capable of maintaining a 1 CFM Air Flow at 10" vacuum."

V. REAGENTS AND MATERIALS

A. Provide a list of all reagents used and specify purity and/or grade.
B. Describe preparation of any special reagents for analysis and sampling.
C. Specify composition, preparation, and concentrations of stock, intermediate, and working standards.
D. Describe in detail any necessary safety precautions for handling and disposition of chemicals.

VI. PROCEDURES

A. FIELD SAMPLING TECHNIQUES

1. Refer to appropriate Field Sampling S.O.P. for exact details of sampling, chain of custody and sample identification procedures.
2. Describe equipment used.
3. List sampling conditions: materials, flow rates, etc.
4. Describe any potential problems and limitations, with means of controlling such problems.
5. Describe any methods used to split samples for other types of analyses, if necessary.

B. LABORATORY SAMPLE PREPARATION/PRETREATMENT TECHNIQUES

1. Describe (or refer to an appropriate section of a Laboratory Quality Control Manual) a protocol for sample log-in procedures, including document control and sample examination for damage. Any possible hazards due to toxic or flammable chemicals must be clearly identified. Any sample storage requirements, such as immediate refrigeration or protection for light must be noted.
2. Describe any methods used for preconcentration, dilution clean-up filtration, extraction, concentration, etc., after the sample is received from the field.

C. ANAYSIS

1. Describe as clearly as possible the exact instrument configuration and set-up techniques
2. Describe analysis blank and calibration procedure with associated limits on precision and accuracy. Describe analysis of Control Samples and limits of the resulting data. Describe steps taken in an "out-of-control" situation. Specify the format and location of recorded calibration and Control Sample data.
3. Describe sample analysis. Description must include an example of expected data (for example, a sample chromatogram with all components of interest labeled).
4. Give calculation procedures for results. Describe data recording and data submittal.

VII. PERFORMANCE CRITERIA

A. Describe frequency of duplicate analyses, spikes, field blanks, and acceptable limits of each.

B. Describe frequency of multiple standard analyses to check method linearity and detection limit.

C. If confirmatory method is used, refer to specific S.O.P.

VIII. METHOD VALIDATION

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, method detection limit and estimated quantitation limit. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time internals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain. The following data will be included in the SOP.

A. A table describing linearity (correlation coefficients), accuracy (method bias), precision (standard deviations at all levels analyzed), and detection.
B. Data on sampling efficiencies, stability, pertinent breakdown products, break through volumes and desorption efficiencies.
C. Data on storage stability and conditions for samples and standards.
D. References to quality assurance information derived from published and/or interlaboratory sources if available.

APPENDIX IV

APPLICATION CHECKLIST

APPLICATION CHECKLIST

1. Pesticide:
2. County:
3. Crop:
4. Field Address:
5. Field Location (R/T/S):
6. Field Size (acres):
7. Contact Person:
8. Background Monitoring Period:
9. Target EQL Met?:
10. Product Applied:
11. Application Rate:
12. Comments on Tank Mix:
13. Method of Application (ground, air, irrigation, injection, tarping etc.):
14. Start of Application:
15. End of Application:
16. Pattern of Application: (e.g., east to west):
17. Weather Conditions:
18. Met Station Location (and elevation):
19. Any Other Applications in Area:
20. Sampler Elevations:

___ Camera pictures of each sampler from all 4 directions
___ Camcorder video of each sampler in relation to field and surroundings
___ Rotameter #s logged
___ Check dimensions of field with known acreage (43560 ft^2/acre) & compare sides
___ Crops around field labeled on diagram

APPENDIX V

FLOW CONTROLLER CALIBRATION FORM

FLOW CONTROLLER; 1-POINT FLOW CALIBRATION SHEET

Project: Pre: _____ Post: _____ **Project #:** _____ **Date:** _____

Desired Flow Rate: _____ **Calib. by:** _____ (name)

BUBBLEMETER READINGS

Controller ID:					
Controller Set:					
-Readings:					
-Readings:					
-Readings:					
Average:					
Deviation:					
Controller ID:					
Controller Set:					
-Readings:					
-Readings:					
-Readings:					
Average:					
Deviation:					

Average of Averages _____ : _____

PROCEDURE

1. Set-up sampler as if to collect sample, including filled sample cartridge.
2. Set flow controller to achieve desired flowrate and record controller setting.
3. Observe and record Bubblemeter flow (on form or direct to floppy - Change File name).
4. Reset to zero. Then repeat step 3 two more times.
5. Calculate the average of 3 readings.
6. Repeat steps 1 thru 5 for each Rotameter.
7. Average of Averages and Deviation automatically calculated. Replace any Rotameters that deviate by 10% or more from the Average of Averages.
8. QA Section will get a copy for comparison with their results for the same setups.

Attachment II

Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Draft
Standard Operating Procedure
Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

05/10/01 version

Approved by:

Mass Spectrometer: Electron Ionization
Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502.

B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps.
2. Whatman filters, 0.45 μm
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps.

C. Reagants

1. Dichloromethane, Pesticide grade or better.
2. Trichloronitromethane, Chem Service PS-4, 98.8%
3. XAD-4 resin sorbent tubes, 400/200mg. SKC, Fullerton, CA.

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at ½ the peak height, 0.60 ± 0.05, and the criteria for relative abundance; 69:100%, 219:100-120%, and 502: 7-12%.

2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interference's. A solvent blank must be analyzed after any sample which may result in possible carry-over contamination.

3. A 5-point calibration curve shall be analyzed with each batch of samples. For the ambient studies the calibration will be 0.5-50.0 ng/mL and for the application studies 50.0-500 ng/mL.

4. A calibration check sample of 7.5 ng/ml is run after the calibration and every 10 samples and at the end of the sample batch. The value of the calibration check must be within $\pm 3\sigma$ (the standard deviation) or ±10% of the expected value whichever is greater. If the calibration check is outside this limit then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.

5. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for trichloronitromethane is calculated by: MDL = 3.14*(std dev values) where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL defined as 5*MDL is 19.8 ng/sample (6.60 ng/mL) based on a 3 ml extraction volume. Results are reported to 3 significant figures above the EQL. Results below EQL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect).

E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD4 tubes (3 at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5 #6-7. The average percent recovery of trichloronitromethane should be $\pm$ 20% of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

F. Storage Stability

Storage stability was set up for a 4 week study. Three (3) XAD4 tubes each were spike at the low and high end concentrations. The tubes were stored in the freezer until analyzed. Table 3 shows the recovery analysis for the samples.

G. Breakthrough

The previous analysis of trichloronitromethane (ARB #A5-169-43) was for 4 hour sampling at 1.0 LPM in September/October, 1986. The current study for ambient monitoring for 24 hours will require a low sample flow rate to meet the requested EQL. Table 2 shows the results of several sampling rates. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling will be at 100 mLpm.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Table 2: Breakthrough Analysis

Flows	Average Primary Bed (ng/ml)	% Primary Recovery/ Standard Dev	Average Secondary Bed (ng/ml)	% Secondary Recovery/ Standard Dev
1.0 LPM	186.8	37.4	81.8	16.4
	(n=8)	3.8		2.4
0.5 LPM	111.8	22.4	89.9	18.0
	(n=2)	1.7		0.9
0.2 LPM	362.6	72.5	36.9	7.4
	(n=3)	1.9		1.3
0.1 LPM	408.4	81.7	<MDL	<MDL
	(n=6)	3.8		

Field Samples spiked at 500 ng/ml.

Table 3: Storage Stability Analysis

Date	Days	XAD Blank	L#1	L#2	L#3	H#1	H#2	H#3
4/4/01	0	<MDL	4.91	5.43	5.2	43.12	43.62	43.31
4/13/01	9	<MDL	6.2	6.06	5.94	43.12	49.34	43.65
4/18/01	14	<MDL	6.71	6.5	6.14	54.38	52.4	54.07
4/24/01	20	<MDL	5.18	6.01	4.57	40.72	41.97	39.12
5/2/01	28	<MDL	5.42	4.26	4.07	43.19	42.66	42.11
Average			5.68	5.65	5.18	44.91	46.00	44.45
Stdev			0.75	0.87	0.88	5.40	4.61	5.66
% Recovery			113.68	113.04	103.68	89.812	91.996	88.904

Attachment III

Application Sampling Procedures
For Adsorbent Tubes

Application Sampling Procedures
For Adsorbent Tubes

Overview:
-Collect samples, according to the schedule in Table 1 of this protocol.

-Collect 4 background samples, from each corner sampling position.

-Collocate 1 field spike with each of the 4 background samples.

-Collect a collocated sample from the downwind site for all sampling periods (except the background period).

-Submit 1 trip blank.

-With the trip blank there should be a total of 59 samples collected during the study, plus 4 trip and 4 field spikes.

--All samples are stored either in an ice-chest on dry ice or in a freezer.

-The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.

-The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples; make and retain copies if desired (not necessary).

Sampling Procedure:
Materials that will be needed to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -zip-lock bags
- -0 to 100 sccpm mass flow meter (MFM) with battery
- -ice chest
- -dry ice

Figure out the route for sampling the 8 locations and try to keep this the same throughout the study.

Preparation and Set-up
On the way to study site, plug the MFM into the battery. It takes the MFMs about 10

minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Set the rotameter roughly to 100 sccpm. Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the 0-100sccpm MFM set the flow rate exactly to 100 sccpm.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, MFM Serial #, any comments and the weather conditions.

Sample collection and Shipment
Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment IV

Field Log Sheet

SAMPLE FIELD LOG SHEET

Project: ChloropicrinApplication Air Monitoring

XAD-4 Tubes

Log #	Sample ID	Date On/Off	Time On/Off	Start Flow (ccpm)	End Flow (ccpm)	Start Leak Check	End Leak Check	Start Count	End Count	Comments	Weather o=overcast pc=partly c=cloudy k=clear	Initials